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Comparison of stable isotope values of Quaternary calcretes from Adana and Mersin provinces: implications on controlling factors

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Abstract: Calcretes are widespread in Adana and Mersin provinces and form under different morphologies. Most calcrete profiles comprise a hard laminated crust/hardpan at the top, gradually intergrading into the nodular and/or tubular/columnar horizon with depth. This study compares the $\delta^{18}O$ and $\delta^{13}C$ values of calcretes from both provinces and discusses the controlling factors and environmental conditions. The $\delta^{18}O$ and $\delta^{13}C$ values are characteristic for the pedogenic calcretes. The Adana calcrete mean $\delta^{18}O$ values of the hardpan, nodules and tubes, and fractures-infills are 0.69‰, 0.77‰, and 1.04‰ PDB heavier than those of the Mersin calcretes, respectively. The overall difference between the two groups is 0.78‰ PDB. The differences are related to the high evaporation rate in Adana province in respect to Mersin province under similar climatic conditions, except for the evaporation rate. The high evaporation rate in Adana province is due to higher ventilation. The $\delta^{13}C$ values of both provinces are almost the same, reflecting calcrete formation in soil with abundant C_3 vegetation similar to contemporary vegetation. In addition, the mean $\delta^{18}O$ and $\delta^{13}C$ values of the hardpan calcretes slightly differ from those of the columnar horizon, showing a depletion in heavy isotopes. The depletion in the mean $\delta^{18}O$ values of hard laminated crust in respect to the columnar horizon is 0.09‰ PDB for Adana calcretes and 0.12‰ PDB for Mersin calcretes. This is related to the relatively thick water film from which the calcretes formed by precipitation and displacive replacement processes. The difference in the mean $\delta^{13}C$ values is 0.32‰ PDB for the Adana calcretes and 0.11‰ PDB for the Mersin calcretes, and the depletion in $\delta^{13}C$ values of the hard laminated crust reflects proximity of the bioactive horizon in the soil.

Key words: Calcrete, stable isotope, hard laminated crust, columnar horizon, southern Turkey

1. Introduction

The calcretes are terrestrial carbonates (predominantly $CaCO_3$) that accumulate and/or replace the host materials in near-surface settings and occur in a variety of morphologies (Wright and Tucker, 1991; Kelly et al., 2000; Alonso-Zarza and Wright, 2010). They are often associated with authigenic clays as a minor constituent, generally including palygorskite and sepiolite (Wang et al., 1994; Verrecchia and Le Coustumer, 1996; Garcia-Romero et al., 2004; Silva et al., 2018; Elidrissi et al., 2018). There are two major groups of calcretes regarding their origin: (i) the pedogenic calcretes, generated by soil-forming processes and characterized by abundant β-fabric (biogenic) features (Klappa, 1983; Shankar and Achyuthan, 2007; Singh et al., 2007; Zamanian et al., 2016; Eren et al., 2018), and (ii) the groundwater or nonpedogenic calcretes, precipitated from groundwater by evaporation in the capillary zone (Goudie, 1973; Nash and McLaren, 2003) or in the phreatic zone (Mann and Horwitz, 1979). Calcretes are widely accepted as indicators of arid and semiarid climates (Anand et al., 1997; Alonso-Zarza and Wright, 2010; Achyuthan et al., 2012). A great number of studies exist on the different aspects of calcretes in the world and also in Turkey, including isotopic studies (e.g., Cerling, 1984; Andrews et al., 1998; Chiquet et al., 2000; Leone et al., 2000; Srivastava, 2001; Achyuthan, 2003; Nash and McLaren, 2003; Dworkin et al., 2005; Durand et al., 2006; Kovda et al., 2006; Achyuthan et al., 2007; Zhou and Chafetz, 2009; Gallala et al., 2010; Meléndez et al., 2011; Horn et al., 2013; Mortazavi et al., 2013; Elidrissi et al., 2017; literature from

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Turkey given in Table 1). However, comparative isotopic studies on calcretes are very limited and include worldwide comparisons (Salomons et al., 1978; Talma and Netterberg, 1983; Eren, 2011). The isotope values of Quaternary calcretes from both Adana and Mersin provinces were previously studied by Kaplan et al. (2014) and Eren et al. (2008). This study aims to compare isotopic compositions of calcretes in these provinces and also attempts to discuss the climatic controlling factors and environmental conditions affecting the formation of "calcrete profiles" (term first used by Meléndez et al. (2011) for the Ebro Basin calcretes and Eren et al. (2018) for the Adana and Mersin calcretes), which has not been undertaken to date. Furthermore, these new regional isotopic comparisons and interpretations will guide future investigations of similar geographic settings concerning paleoclimate and the environmental conditions in the Mediterranean and worldwide.

2. Geological setting

This study concerns the Neogene Adana basin developed within the central Taurides of SE Turkey and comprises two sampling sites in Adana and Mersin provinces (Figure 1). The basin infill contains Tertiary and Quaternary sedimentary rocks and sediments unconformably overlying the pre-Miocene basement rocks of clastics, carbonates,

Table 1. Literature summary of the calcretes in Turkey.

Reference	Subject	Location
Kapur et al., 1987	Soil-calcrete (caliche) and its relationship with geomorphology	Adana
Özer et al., 1989	ESR and TL age determination of caliche nodules	Çukurova/Adana
Kapur et al., 1990	Geomorphology and pedogenic evolution of Quaternary calcretes	Adana
Kapur et al., 1993	Soil stratigraphy and Quaternary caliche	Misis/Adana
Atalay, 1996	Paleosols as indicators of the climatic changes	South Anatolia
Atabey et al., 1998	Sedimentology of caliche (calcrete) occurrences	Kırşehir
Kapur et al., 2000	Carbonate pools in soils	Mediterranean area
Eren, 2007	Genesis of tepees in the Quaternary hardpan calcretes	Mersin
Eren et al., 2008	Quaternary Calcrete Development	Mersin
Kadir and Eren, 2008	Genesis of clay minerals in Quaternary caliches	Mersin
Kadir et al., 2010	Dolocretes and associated palygorskite	Çanakkale
Eren and Hatipoğlu-Bağcı, 2010	Karst surface features of the hard laminated crust (caliche hardpan)	Mersin
Eren, 2011	Stable isotope geochemistry of Quaternary calcretes	Mersin
Küçükuysal et al., 2011	ESR dating of calcrete nodules	Bala/Ankara
Kaplan et al., 2013	Mineralogical, geochemical, and isotopic characteristics of Quaternary calcretes	Adana
Kadir et al., 2014	Genesis of Late Miocene-Pliocene lacustrine palygorskite and calcretes	Kırşehir
Kaplan et al., 2014	Pedogenic palygorskite associated with Quaternary calcretes	Adana
Küçükuysal et al., 2013	Multiproxy evidence of Mid-Pleistocene dry climates in calcretes	Ankara
Küçükuysal and Kapur, 2014	Mineralogical, geochemical, and micromorphological evaluation of the Plio-Quaternary paleosols and calcretes	Karahamzalı/Ankara
Küçükuysal, 2016	Mineralogical, micromorphological, geochemical, and stable isotopic compositions, and radiocarbon ages of the Late Pleistocene calcretes	Gölbaşı Basin/Central Anatolia
Gürel and Özcan, 2016	Paleosol and dolocrete associated clay mineral	Tuzgölü/Ankara
Kadir et al., 2018	Genesis of palygorskite and calcrete in Pliocene Basin	Eskişehir
Eren et al., 2018	Biogenic (β-fabric) features in the hard laminated crusts	Adana, Mersin

Modified from Eren et al. (2018).

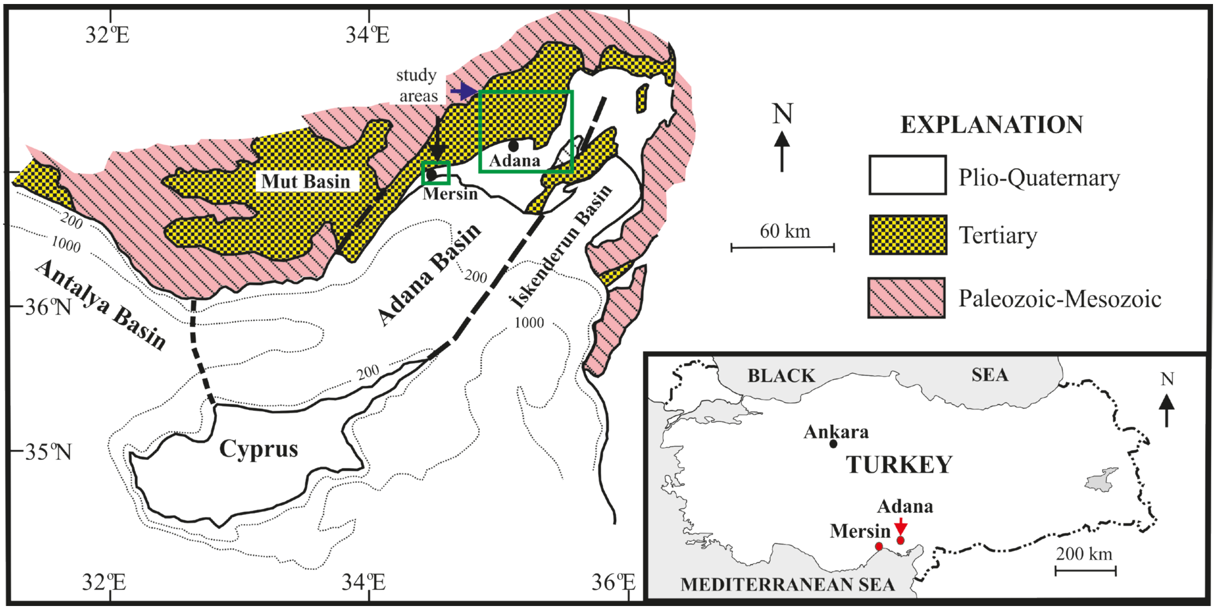

Figure 1. Location map illustrating parts of the study area in the Adana Basin (modified from Yalçın and Görür, 1983).

and ophiolites (Figures 2 and 3; Schmidt, 1961; Yalçın and Görür, 1983; Yetiş, 1988; Yetiş et al., 1995; Darbaş et al., 2008). The Tertiary units are mainly represented by the Kuzgun and Handere Formations in Mersin and Adana provinces, respectively. The Kuzgun Formation, deposited during the late Miocene (Tortonian), comprises predominantly shallow marine mudstones and sandstones at the lower to middle part and fluvial deposits consisting mainly of reddish-brown mudstones of overbank deposits intercalated with cross-bedded sandstones of point bar and channel deposits at the upper part (Eren et al., 2008). The Handere Formation of the Messinian to Pliocene age is made up of predominantly mudstones associated with conglomerates, sandstones, and gypsum lenses of lagoonal, shallow marine, and fluvial environments (Yetiş et al., 1995; Gürbüz, 1999). The Quaternary covers recent alluvium, alluvial terraces, colluvial red soils, and/or red soils and hardpan calcretes.

Calcretes are widely available on and/or within layers of the Kuzgun and Handere Formations in Mersin and Adana provinces, respectively (Figure 4; Eren et al., 2008; Kaplan et al., 2013). They have also been recognized in/on the Pleistocene glacis (mass flow or mud flow) terraces (Kapur et al., 1993; Kaplan et al., 2013) of Adana province and the Quaternary colluvial red soils of Mersin province (Eren et al., 2008). The Pleistocene ages of the calcretes of the area dated from 250 to 782 ka BP were determined by Özer et al. (1989), whereas the early Holocene to Pleistocene ages were based on the field observations of Erol (1981, 1984), Atalay (1996), Eren et al. (2008), and Kaplan et al. (2013) studies. Furthermore, Küçükuysal et al. (2011) and Küçükuysal (2016) provided Middle to Late Pleistocene age for calcretes determined by ESR and radiocarbon techniques in the Bala and Gölbaşı Basin/Ankara regions of central Turkey, respectively.

Calcrete profiles often reflect maturation in the soil profile development and consist mainly of the hard laminated crust with a thickness of about 1.5 m at the top, gradually intergrading with depth into the 1.5–2 m thick nodular and/or tubular/columnar (term first used by Kapur et al., 1990) horizon (Figure 4; Eren et al., 2008; Kaplan et al., 2013). In some cases, fracture infills are also observed in the nodular-tubular horizons. The hard laminated crust spreads in large areas unconformably overlying the different layers of the Handere and Kuzgun Formations and outcrops as an undulating crust on the small ridges and highs in low-lying areas (20 to 250 m). The nodular and/or tubular/columnar horizon has developed predominantly within the mudstones of the Kuzgun and Handere Formations as scattered/discreet white mottlings associated with fracture infills.

3. Materials and methods

A total of 164 calcrete samples were collected from 24 measured sections in Adana and Mersin provinces. For isotope analysis, 24 calcrete samples were selected from the hard laminated crust (n = 25) and nodular and/or tubular/columnar horizon (n = 19). Isotopic measurements were

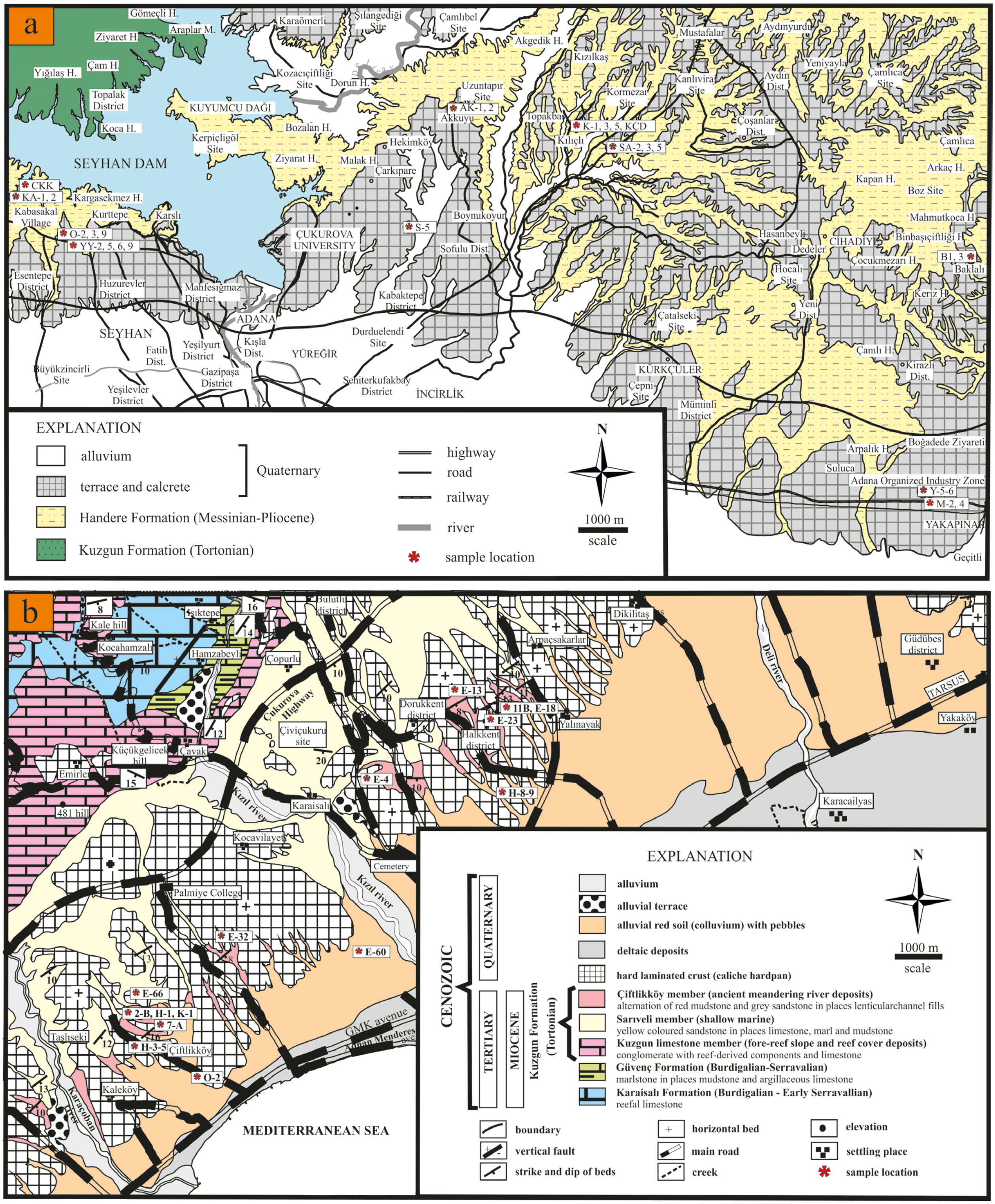

Figure 2. Geological maps of the studied areas: (a) the Adana region (modified from Yetiş, 1988); (b) the Mersin area (Eren et al., 2004).

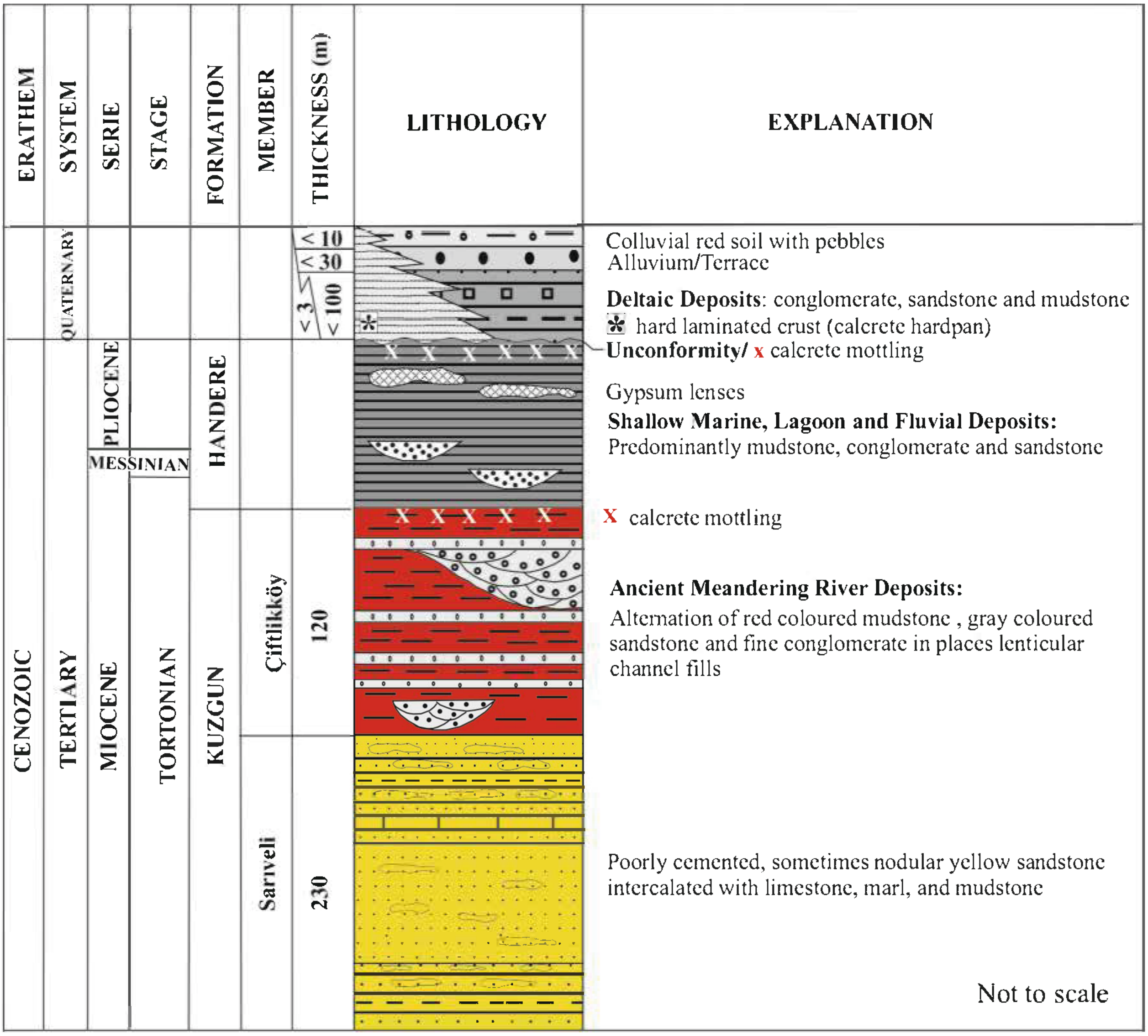

Figure 3. Generalized stratigraphic column for the studied areas (modified from Eren et al., 2018).

made on carbon dioxide (CO_2) released after the reaction of approximately 5 mg of powder samples with 100% phosphoric acid (H_3PO_4) at 50 °C using a Finnigan MAT 252 mass spectrometer at ISO Analytical Laboratories (Cheshire, UK). The mass spectrometer was calibrated using NBS 18 and NBS 19 standards. The isotopic results were reported as δ values in parts per mil relative to the Pee Dee Belemnite (PDB) standard. Analytical detection limits at laboratory conditions were ±0.05‰ for $\delta^{18}O$ and ± 0.02‰ for $\delta^{13}C$.

The analytical results were cross-plotted as $\delta^{18}O$ versus $\delta^{13}C$ and analyzed using multivariate statistical analysis to illustrate separation in the samples. Hierarchical clustering analysis (HCA) methods were used for all samples, and the Ward method revealed more meaningful cluster structures (Ward, 1963). The dendrograms were drawn over the statistical application and the Ward method in turn minimizing intracluster differences yielded the correct results. The two-dimensional Pythagorean theorem of the Euclidean distance was used for the calculations (Kaufman and Rousseeuw, 2009).

4. Results

Isotope values of the calcretes are listed in Table 2, where samples of the Mersin calcretes have $\delta^{18}O$ and $\delta^{13}C$ values ranging from −4.31‰ to −5.84‰ and from −8.40‰ to

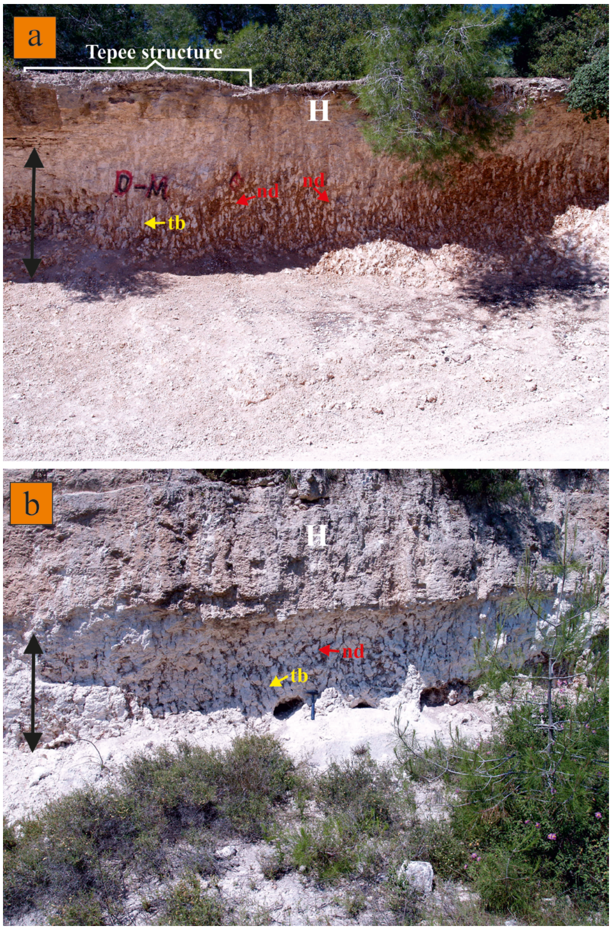

Figure 4. Typical calcrete profiles: (a) Kılıçlı village, Adana; (b) Mersin University campus area, Mersin, showing the hard laminated crust (H) at the upper part of the profile gradually intergrading downward into the nodular (nd) and tubular (tb) horizon (black arrow). In (a), the hard laminated crust shows an upward buckling, which is the cross-section of dome-lime surface morphologies called tepee structure (Eren, 2007).

–9.65‰ PDB, respectively. The Adana calcretes have PDB values of $\delta^{18}O$ ranging from –3.76‰ to –5.74‰ and of $\delta^{13}C$ ranging from –7.71‰ to –10.01‰. In this context, the $\delta^{18}O$ values of calcretes vary in a wide range in respect to the $\delta^{13}C$ values in the Mersin area, whereas the Adana calcretes have $\delta^{18}O$ and $\delta^{13}C$ values varying almost in the same range (Figure 5). Within this scope, both cross-plot and hierarchical cluster analyses of $\delta^{18}O$ and $\delta^{13}C$ values show two distinct calcrete groups referring to Adana and Mersin provinces (Figures 5 and 6). Consequently, the hierarchical cluster analysis revealed that the fracture infills, separately sampled in the field, are associated with and appear to be a subgroup of the calcrete nodules/tubes of the columnar horizon (Figure 6).

5. Discussion

The isotope values of the calcrete samples collected from the hard laminated crust and the nodular and/or tubular horizon, including the fracture infills, are in the range of $\delta^{18}O$ and $\delta^{13}C$ for the pedogenic calcretes (Alonso-Zarza, 2003; Bajnóczi et al., 2006; Eren, 2011; Küçükuysal, 2016). Eren (2011) and Küçükuysal (2016) provided worldwide and mainly regional isotopic comparisons of calcretes, respectively. These $\delta^{18}O$ and $\delta^{13}C$ values reflect calcrete development under the influence of meteoric water and soil-forming processes, respectively (Purvis and Wright, 1991; Strong et al., 1992; Leone et al., 2000; Alonso-Zarza, 2003; Alonso-Zarza and Arenas, 2004; Eren, 2011). The oxygen isotopic fractionation during inorganic calcite precipitation depends mainly on temperature; therefore, $\delta^{18}O$ values reflect the temperature of water from which calcite was precipitated (Friedman and O'Neil, 1977; Talbot and Kelts, 1990; Bar-Matthews et al., 2003; Dietzel et al., 2009), whereas the $\delta^{13}C$ values of the pedogenic carbonates are directly related to the soil-derived CO_2 and infer the plant types living at the surface during formation of the calcretes. There are two major plant photosynthetic pathways, C_3 and C_4, where each pathway fractionates carbon to a different extent (Alonso-Zarza, 2003; Tanner, 2010). Moreover, comparisons of the isotopic results using the cross-plot and hierarchical cluster analysis exhibit two distinct groups of Adana and Mersin provinces (Figures 5 and 6). The Adana calcrete samples exhibit an enrichment in $\delta^{18}O$ values compared to the values of the Mersin calcrete samples. These enrichments in the mean $\delta^{18}O$ values of the hard laminated crust, calcrete nodules and tubes, and fracture infills are 0.69, 0.77, and 1.04, respectively. The enrichment is clearer in the fracture infill samples. The overall enrichment in mean $\delta^{18}O$ values of the two groups is 0.78‰ PDB. The oxygen isotopes of the calcretes are sensitive to climatic conditions and mainly reflect the composition of meteoric water (Talma and Netterberg, 1983; Alonso-Zarza, 2003). The enrichment in the $\delta^{18}O$ values of the Adana region was related to the high evaporation rate in comparison to the Mersin area, despite similar climatic conditions (Table 3). The high evaporation rate of the Adana region is due to probable higher ventilation rates of the area that resulted in removal of moisture in the air and consequently enhanced the evaporation rate under the same annual average temperature conditions as the Mersin area. High mean $\delta^{18}O$ values in the samples of fracture infills are due to the appropriate connection of the fractures with the air spaces with respect to the soils and their high moisture rates. The almost identical $\delta^{13}C$ values, together with the abundant β-fabric (biogenic) features in the hard laminated crust (Eren et al., 2008, 2018; Kaplan et al., 2013) of both provinces are indicators

Table 2. Isotopes of the calcretes from the Adana and Mersin provinces.

Adana province			Mersin province		
Sample	δ^{18}O (‰ PDB)	δ^{13}C (‰ PDB)	Sample	δ^{18}O (‰ PDB)	δ^{13}C (‰ PDB)
Hard laminated crust			Hard laminated crust		
Y-6	–3.76	–10.01	H-1	–5.26	–9.00
O-9	–4.64	–8.55	H-3	–4.92	–8.89
YY-5	–4.50	–9.09	H-4	–4.89	–8.66
CKK	–5.74	–8.86	H-5	–4.97	–9.03
B-3	–3.95	–8.41	H-8	–5.25	–9.07
K-1	–4.61	–8.41	H-9	–5.25	–8.90
M-4	–3.91	–8.75	E-4	–5.47	–8.49
KA-2	–5.13	–9.15	E-13	–5.84	–8.91
SA-5	–4.35	–8.27	E-66	–5.31	–8.56
AK-2	–4.91	–8.34	Mean	–5.24	–8.83
Mean	–4.55	–8.78			
Nodule and tube			Nodule and tube		
Y-5	–3.87	–9.38	7-A	–5.13	–8.70
O-2	–4.44	–8.63	11-B	–5.39	–8.79
O-3	–4.53	–8.77	O-2	–5.07	–8.61
YY-9	–4.22	–8.35	E-18	–5.58	–8.63
B-1	–4.13	–8.38	E-32	–5.59	–8.40
K-3	–4.30	–8.25	12	–5.43	–8.66
K-5	–4.56	–8.11	E-60	–4.31	–9.65
M-2	–3.87	–8.24	2-B	–4.56	–8.43
KA-1	–4.69	–8.71	Mean	–5.13	–8.73
SA-2	–4.66	–7.94			
SA-3	–4.68	–8.22			
S-5	–4.04	–8.53			
AK-1	–4.77	–8.49			
Mean	–4.36	–8.46			
Fracture infill			Fracture infill		
KCD	–4.05	–7.71	E-23	–5.00	–8.54
YY-2	–4.06	–8.51	K-1	–5.18	–8.74
YY-6	–4.04	–8.26	Mean	–5.09	–8.64
MNean	–4.05	–8.16			

See Figure 2 for sample locations.

of pedogenesis (Eren et al., 2008; Eren, 2011; Kaplan et al., 2013). Similarities in δ^{13}C values between the two groups also reflect the development of calcretes under the same vegetation cover. Small variations in the δ^{13}C values are due to the soil respiration rate in local areas (Cerling, 1984; Andrews et al., 1998). The δ^{13}C values suggest the influence of dense C_3 vegetation on calcrete development (Lee, 1999; Bar-Matthews et al., 2003; McDermott, 2004; Candy et al., 2012; Alçiçek and Alçiçek, 2014). Moreover, similarities in the contemporary and past climatic

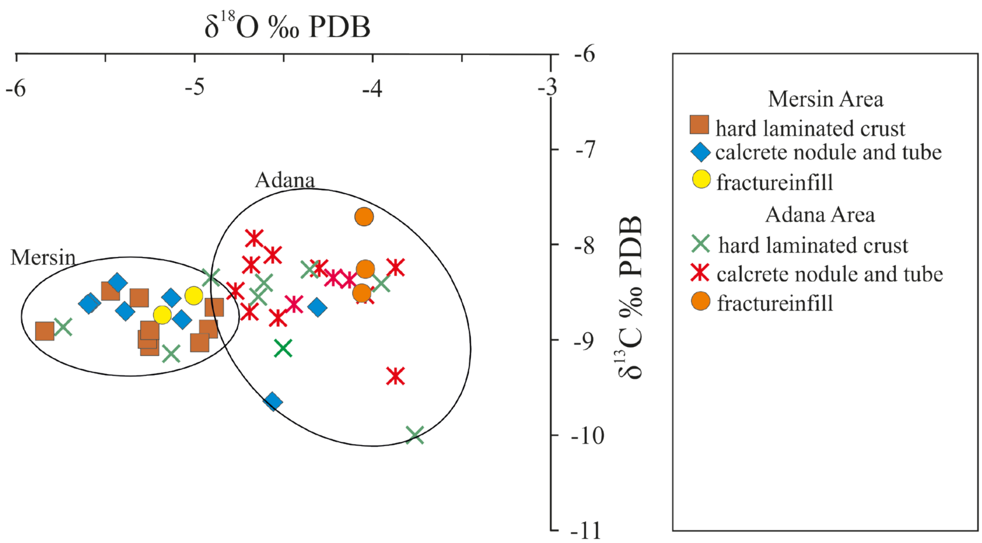

Figure 5. A cross-plot of stable isotope values ($\delta^{18}O$ and $\delta^{13}C$) of the calcretes showing the two distinct groups of Adana and Mersin provinces.

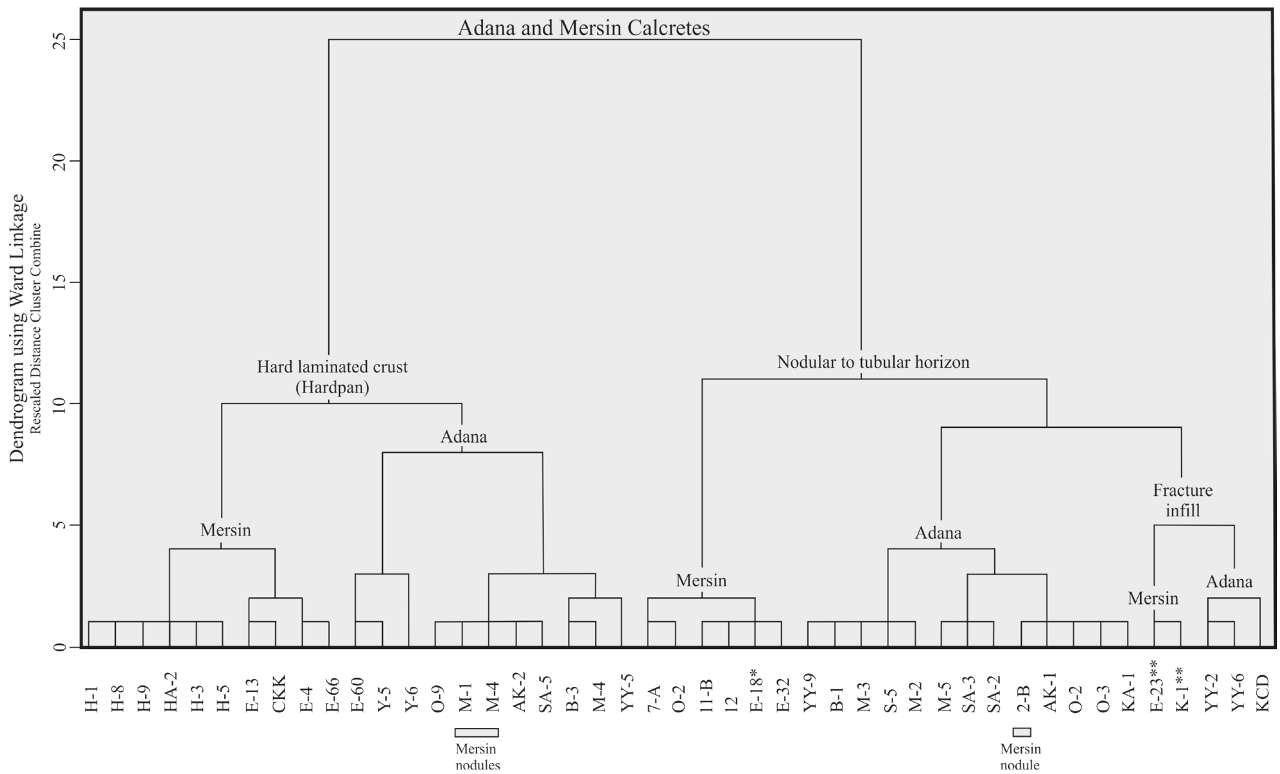

Figure 6. Cluster analysis showing two groups of samples of Adana and Mersin provinces where the fracture infills appear as a subgroup of the nodular-tubular horizon.

Table 3. Climatic properties for Adana and Mersin provinces from the Turkish State Meteorological Service (https://www.mgm.gov.tr/).

Data	Adana	Mersin
*Mean annual temperature (°C)	18.9	19.1
*Mean annual precipitation (mm)	646.6	634
**Mean annual evaporation (mm)	1555.3	1262.2
**Mean annual humidity (%)	65.54	60.78

* From 1927 to 2017; ** from 2007 to 2017.

conditions suggest the availability of similar contemporary vegetation represented by the Mediterranean crops on the appropriate land surfaces, namely olives (*Olea europaea*) and carob (*Ceratonia siliqua*), including other shrubby vegetation. The end-member $\delta^{13}C$ values of soil carbonates formed under 100% C_4 and C_3 ecosystems are about 0‰ to +3‰ and −12‰ to −13‰ PDB, respectively (Cerling, 1984; Cerling et al., 1989; Zamanian et al., 2016).

The $\delta^{18}O$ and $\delta^{13}C$ values of the hardpans also differ slightly from those of the nodular and/or tubular horizons. The hard laminated crust shows a slight depletion in the $\delta^{18}O$ values regarding those of the calcrete nodules and tubes. These values are 0.19‰ PDB for the Adana calcretes and 0.11‰ PDB for the Mersin calcretes. The depletion in the $\delta^{18}O$ values is due to leaching soil water along pore channels, from or in which calcite forms by precipitation and displacive replacement processes. During the early stages of calcrete profile development, the nodular and tubular features form from the vertically leaching, relatively thin soil-water cover, reducing the permeability of rocks and sediments, in turn causing the development of sheet-like laminar calcretes on the impermeable horizon from laterally moving, relatively thick soil-water (Figure 7; Wright et al., 1988, 1995; Eren et al., 2008; Kaplan et al., 2014). This assumption is also supported by the existence of palygorskite in the samples of calcrete nodules and tubes, and its absence in the hard laminated crust. Palygorskite precipitation requires high pH values (pH » 9; Verrecchia and Le Coustumer, 1996; Bouza et al., 2007) or more evaporative conditions with respect to calcite (Eren et al., 2008, 2018; Kaplan et al., 2013, 2018). A slight difference is present between the average values of the hard laminated crust and nodular and/or tubular horizon regarding the $\delta^{13}C$ values. This difference is 0.32‰ PDB for the Adana calcretes and 0.10‰ PDB for the Mersin calcretes. The hard laminated crust exhibits a depletion in the $\delta^{13}C$ values related to proximity to the bioactive horizon in the soil (Gong et al., 2005). The nodular and/or tubular horizon develops below the bioactive soil horizon where water is leached vertically in a vadose zone from which calcite precipitates or replaces the host material, creating impermeable/water plugged conditions. This characterizes the early stage of the calcrete profile development in the region (Eren et al., 2008, 2018; Kaplan et al., 2013). The advanced stage most likely occurred over this nodular

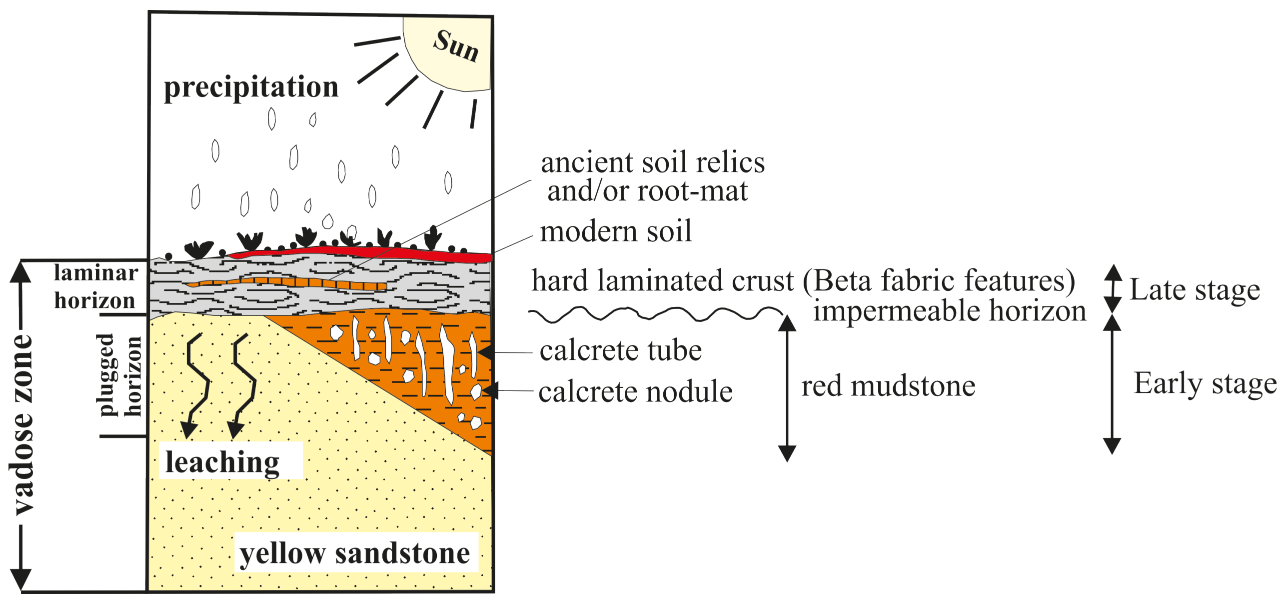

Figure 7. Schematic presentation of the calcrete development exhibiting two major stages: (i) early stage characterized by calcrete mottling, and (ii) late stage characterized by lamination (modified from Eren et al., 2018).

and/or tubular horizon close to the bioactive soil horizon where the static soil water probably rested laterally over the impermeable column horizon. This consequently increased the residence time of water in the bioactive layer and most likely influenced the soil light carbon isotopes (Figure 7).

6. Conclusion

The oxygen and carbon isotopes of the calcretes in Adana and Mersin provinces indicate a pedogenic origin similar to calcretes in other parts of the world. The enrichment of $\delta^{18}O$ values of the calcretes in Adana province in respect to those in Mersin caused by the high evaporation rate in the Adana region is bound to higher ventilation of the land surface. The $\delta^{13}C$ values suggest that calcrete formation in the soil is associated with extensive C_3 vegetation similar to contemporary Mediterranean-type vegetation. Isotopic difference is also present between the hardpan and nodular and/or tubular/columnar horizon. The hardpan exhibits a slight depletion in the $\delta^{18}O$ and $\delta^{13}C$ values with respect to those of the nodular and/or tubular/columnar horizon. This is most likely due to the amount of leaching soil water from which calcretes form during the pedogenic processes, as well as the proximity to the bioactive soil layer.

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